

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : **2004-047206**

(43)Date of publication of application : **12.02.2004**

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(51)Int.Cl. H01M 8/02

C25D 11/00

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## **(54) ELECTROLYTE FILM FOR FUEL CELL**

### **(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide an electrolyte film for a fuel cell with high proton selectivity using hydrogen or methanol as fuel that can be used in a temperature of  $\geq 100^{\circ}\text{C}$ .

**SOLUTION:** The electrolyte film is characterized in that it has a through-hole with a diameter of 0.01-150 $\mu\text{m}$  formed by carrying out anodic oxidation on a metal film or silicon film, and the inner wall of the through hole is modified by a proton conductive functional group. It is favorable that an OH group is used as a functional group. A material that is used for the metal film allows the formation of the through hole by anodic oxidation. Preferably, it is aluminum, titanium, zinc, indium, or an alloy having them as a principal component.

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## **LEGAL STATUS**

[Date of request for examination] 26.11.2004

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]

It is used inside the fuel cell which is capturing the spotlight especially recently because energy generation effectiveness is high.

[0002]

[Description of the Prior Art]

A fuel cell is classified into four kinds according to the class of electrolyte used. It is with a solid acid ghost form fuel cell (SOFC) and a solid-state macromolecule form fuel cell (PEFC) to be classified according to in these four kinds as what is used in a moderate temperature field from a low-temperature field. Moreover, since electrolytic immobilization is easy for these, application to a mobile is also possible, an interest is attracted most and expansion of applicability is considered recently.

[0003]

In PEFC, the application as a power source for a small home power source, a portable power source, and mobiles is being developed using the output in low temperature being large, but on the other hand, development of the ion-selective polyelectrolyte film with unnecessary moisture management with high thermal resistance is called for. Moreover, although the expectation as a power source for pocket devices is growing since the thing of a type which reforms a methanol fuel directly within a cell and obtains hydrogen is easy to miniaturize, the endurance over a methanol is high and development of the polyelectrolyte film with high ion selectivity is called for.

[0004]

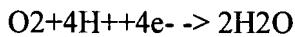
By the way, the fuel cell consists of an anode pole (fuel electrode), a cathode pole (air pole), and an electrolyte membrane fundamentally. It was quoted and shown in drawing 1 from "technical trend investigation about a fuel cell" according [ accord / PEFC / an example ] the structure and the principle of operation of a fuel cell to a technical inquiry section, the Patent Office. The laminating of the separator as the gaseous diffusion layer and charge collector of hydrogen which is the catalyst and fuel which take an electron from hydrogen and form a proton is carried out, and the anode is constituted. Moreover, the laminating of the catalyst, the diffusion layer of air, and separator to which the reaction of a proton and oxygen is made to perform is carried out, and the cathode is constituted. Generally as for the electrolyte membrane, the polyelectrolyte film of proton conductivity of a sulfonic-acid system is used. The reaction in each electrode is as follows.

[0005]

Anode reaction

$H_2 \rightarrow 2H^{++} + 2e^-$

Cathode reaction



Proton conductivity solid-state poly membranes, such as a perfluoro sulfonic acid (trade name: product made from Nafion DuPont), etc. are one of those which were well known as polyelectrolyte film for PEFC. Many through tubes which are the diameters of about 100nm for which OH-radical of isolation was prepared in that wall are prepared in such film, and it is characterized by making a proton penetrate from an anode side to a cathode side by this OH-radical. However, it is known that such film makes not only a proton but the hydrogen content child who is a raw material, a methanol, etc. penetrate to a cathode side. The fuel and oxidizer which were supplied when such a thing broke out cannot carry out a direct reaction by the cathode side, and cannot output energy as power. Therefore, the problem that the stable output cannot be obtained arises.

[0006]

There is proton conductivity film (electrolyte membrane) indicated by JP,2002-110200,A as what solves such a trouble. This proton conductivity film aims at controlling that a methanol penetrates this film, maintaining proton conductivity.

[0007]

Specifically, it is characterized by being the complex of the complex of a proton conductivity polymer and a specific polymer, or the copolymer of a proton conductivity polymer, a specific polymer, and one oxide of the groups of Ti, Zr, aluminum, B, Mo, W, Ru, Ir, germanium, or V.

[0008]

Although proton selectivity is improved to be sure, since an ingredient is a macromolecule or a macromolecule subject like said Nafion, this proposed electrolyte membrane has the fault of not being made to an elevated temperature 100 degrees C or more. For this reason, it is applicable to the home stationing mold with which the specification of a steam is examined for the effectiveness rise. In addition, service temperature is considered to be 150-250 degrees C in this case.

[0009]

[Problem(s) to be Solved by the Invention]

The place which this invention is made in view of the above-mentioned situation, and is made into the purpose is offer of the electrolyte membrane for fuel cells usable at the temperature of 100 degrees C or more with high and proton selectivity in the electrolyte membrane for fuel cells which uses hydrogen or a methanol as a fuel.

[0010]

[Means for Solving the Problem]

This invention which solves the above-mentioned technical problem has diameter the through tube of 0.01-150 micrometers prepared by anodizing a metal membrane or the silicon film, and is characterized by embellishing the functional group of proton conductivity in the wall of this through tube.

[0011]

Moreover, as a functional group of this invention, an OH radical is desirable.

[0012]

What can be used as the metal membrane quality of the material of this invention can form a through tube by anodic oxidation. It is the alloy which makes aluminum, titanium, zinc, an indium, and these a principal component more preferably.

[0013]

[Embodiment of the Invention]

This invention is the electrolyte membrane for fuel cells which has diameter the through tube of 0.01-150 micrometers prepared by anodizing a metal, and embellished the functional group of proton conductivity in the wall of this through tube. While maintaining proton selectivity highly by carrying out like this, thermal resistance is raised and it becomes possible to use 100 degrees C or more as the electrolyte membrane which can specifically use a steam.

[0014]

If the thing using the electrolyte membrane of this invention is said by the conventional classification, it will serve as PEFC and an intermediate type of SOFC. Conventionally, in PEFC, coexistence of moisture is indispensable, therefore the limitation was in service temperature in the fuel cell. However, in this invention, by selecting the class and tight ness of a functional group of an electrolyte membrane, coexistence of water stops becoming indispensable and serves as a very realistic fuel cell.

[0015]

Moreover, if the electrolyte membrane of this invention is used, since the fuel cell which can be used to an elevated temperature 100 degrees C or more can be created, it becomes usable also as a fixed mold fuel cell in the object for mount, or a home.

[0016]

By this invention, an electrolyte membrane is created by anodic oxidation of a metal membrane or the silicon film because [ of the heat-resistant improvement in the film ]. What can be used as a metal membrane must be what can form a through tube with a diameter of 0.01-150 micrometers by anodic oxidation. It is more desirable than a handling low price, economical efficiency, etc. to use aluminum, titanium, zinc, and the alloy that makes an indium and these a principal component as a metal membrane ingredient. Although a through tube is prepared in such a metal membrane and silicon film according to electrolytic oxidation, the diameter of a through tube is possible by adjusting anodic oxidation conditions, such as an electrical potential difference, an electrode spacing, time amount, and an acid type.

[0017]

In addition, anodic oxidation makes a metal membrane and the silicon film an anode plate, and direct current voltage is impressed in water or the electrolytic solution. At this time, while oxygen usually occurs, according to an electrical potential difference, an acid type, time amount, etc., the through tube of the diameter of a request carries out self-alignment tidily in an anode plate at spacing which is about several 10-100nm.

[0018]

By the way, if the diameter of a through tube is too small, although proton selectivity will improve, passage resistance becomes large, and the function as a cell falls. Moreover, since hydrogen and the methanol used as a raw material will also be passed although passage resistance of a proton decreases if it becomes large on the contrary, a cell property falls. From such a thing, the function as a filter will also be required of an electrolyte membrane. That is, to determine the diameter of a through tube with a raw material is desired. Therefore, although the path near 150nm is sufficient when using a raw material with big molecule size, in the case of a raw material with small molecule size, dozens of nm or less is needed. the need of being referred to as 0.01-1nm when using hydrogen as a raw material -- things are desirable.

[0019]

The functional group of proton conductivity is embellished in an inner-wall-of-through-hole side. As a functional group, it is simple to choose an OH radical, and it is good. Moreover, since

spacing of an OH radical is made densely, it can make transfer of a proton good.

[0020]

When a functional group attaches and aluminum is chosen, for example as an electrolyte membrane ingredient as a direction, the front face which includes an inner-wall-of-through-hole side according to electrolytic oxidation is covered with the alumina film. In the case of the alumina film, it is possible to embellish an anion and a cation bordering on the pH= abbreviation 9. Because, pH is charged in  $\text{AlO}_2^-$  in nine or more abbreviation, and an alumina film front face is charged in  $\text{aluminum}^{3+}$ , when pH is less than abbreviation 9. Therefore, pH is made less than into nine and an OH radical is supplied to an alumina front face.

[0021]

The aluminum film after electrolytic oxidation is first immersed in ion exchange water, into ion exchange water, a nitric acid is added and, specifically, pH is lowered to about four. Then, aqueous ammonia is dropped into ion exchange water, pH is returned to 7, and ion exchange water is exchanged and washed.

[0022]

In addition, when the alumina front face is dry, a good result will be obtained, if the above-mentioned actuation is tried after applying and humidifying steam on this front face.

[0023]

Moreover, if not only an OH radical but a catalyst bed is applied to an inner-wall-of-through-hole side, it is possible it not only does not to let a big molecule pass, but to disassemble a raw material to a proton inside an electrolyte membrane through tube.

[0024]

[Example]

Next, this invention is further explained using an example.

(Example 1)

Creation of the electrolyte membrane 1 made from an alumina which obtained the sample 1-base material as aluminum

Aluminium foil with width of face of 50mm, a die length [ of 50mm ], and a thickness of 15 micrometers was made into the anode plate, platinum was used as cathode, using the oxalic acid solution of concentration 0.3 mol/l as the electrolytic solution, potentiostatic electrolysis was carried out on the electrical potential difference of 40 volts, and electrolytic oxidation of the aluminum was carried out.

[0025]

after [ of energization initiation ] several seconds, although the current value became about 1 law by 50mA, it was substantially set to 0mA after about 60 minutes. The anode plate was pulled up and rinsed after that, it exfoliated, the film was dipped in the mixed acid (6wt% sulfuric-acid +1.8wt% hydrochloric acid) about dozens seconds, and it washed in cold water immediately. The diameter of the obtained through tube was about 70nm.

[0026]

Then, the anode plate front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-of-through-hole side.

[0027]

Creation of the electrolyte membrane 2 made from an alumina which obtained the sample 2-base material as aluminum

Aluminium foil with width of face of 50mm, a die length [ of 50mm ], and a thickness of 15

micrometers was made into the anode plate, platinum was used as cathode, using the oxalic acid solution of concentration 0.3 mol/l as the electrolytic solution, potentiostatic electrolysis was carried out on the electrical potential difference of 50 volts, and electrolytic oxidation of the aluminum was carried out.

[0028]

after [ of energization initiation ] several seconds, although the current value became about 1 law by about 60mA, it was substantially set to 0mA after about 60 minutes. The anode plate was pulled up and rinsed after that, it exfoliated, the film was dipped in the mixed acid (6wt% sulfuric-acid +1.8wt% hydrochloric acid) about dozens seconds, and it washed in cold water immediately. The diameter of the obtained through tube was 50nm.

[0029]

Then, the anode plate front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-of-through-hole side.

[0030]

Creation of the electrolyte membrane 3 made from an alumina which obtained the sample 3-base material as aluminum

Aluminium foil with width of face of 50mm, a die length [ of 50mm ], and a thickness of 15 micrometers was made into the anode plate, platinum was used as cathode, using the oxalic acid solution of concentration 0.3 mol/l as the electrolytic solution, potentiostatic electrolysis was carried out on the electrical potential difference of 40 volts, and electrolytic oxidation of the aluminum was carried out.

[0031]

after [ of energization initiation ] several seconds, although the current value became about 1 law by 50mA, it was substantially set to 0mA after about 60 minutes. The anode plate was pulled up and rinsed after that, it exfoliated, the film was dipped in the mixed acid (6wt% sulfuric-acid +1.8wt% hydrochloric acid) about several seconds, and it washed in cold water immediately. The diameter of the obtained through tube was about 1 nm.

[0032]

The anode plate was pulled up after that and ion exchange water washed. Then, the anode plate front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-of-through-hole side.

[0033]

Creation of the electrolyte membrane 4 made from an alumina which obtained the sample 4-base material as aluminum

Aluminium foil with width of face of 50mm, a die length [ of 50mm ], and a thickness of 15 micrometers was made into the anode plate, platinum was used as cathode, using an oxalic acid solution with a concentration of 0.3 mols [ /l. ] as the electrolytic solution, potentiostatic electrolysis was carried out by electrical-potential-difference 40V, and electrolytic oxidation of the aluminum was carried out (it is the same as data 1).

[0034]

The film finally obtained was dipped in the mixed acid (6wt% sulfuric-acid +1.8wt% hydrochloric acid) about 1 second, and it washed in cold water immediately. Consequently, when the detailed hole got bored with the last edge of pore and having been measured in TEM, the diameter of the obtained through tube was about 0.5nm.

[0035]

The anode plate was pulled up after that and ion exchange water washed. Then, the anode plate front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-of-through-hole side.

[0036]

It is creation of the electrolyte membrane made from titanium \*\*\*\* titanium oxide about a sample 5-base material.

Width of face 50mm, die length 50mm and a titanium foil with a thickness of 15 micrometers are made into an anode plate, platinum is used as cathode, and it is concentration as the electrolytic solution. A 0.5 mols [1. ] oxalic acid solution is used, and it is an electrical potential difference. Potentiostatic electrolysis was carried out by 60 volts, and electrolytic oxidation of the titanium foil was carried out. The diameter of the obtained through tube was about 50nm.

[0037]

Several energization initiation second aftercurrent value Although 45mA was shown, it was substantially set to 0 after 65 minutes. The anode plate was pulled up after that and ion exchange water washed. Then, the anode plate front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-of-through-hole side.

[0038]

Creation of the electrolyte membrane made from a zinc oxide which obtained the sample 6-base material as zinc

Width of face 50mm, die length 50mm and a zinc foil with a thickness of 15 micrometers are made into an anode plate, platinum is used as cathode, and it is concentration as the electrolytic solution. A 0.5 mols [1. ] oxalic acid solution is used, and it is an electrical potential difference. By 50 volts, potentiostatic electrolysis was carried out and zinc Tomari electrolytic oxidation was carried out. The diameter of the obtained through tube was about 45nm.

[0039]

Several energization initiation second aftercurrent value Although 50mA was shown, it was substantially set to 0 after 50 minutes. The anode plate was pulled up after that and ion exchange water washed. Then, the anode plate front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-of-through-hole side.

[0040]

Creation of the electrolyte membrane made from indium oxide which obtained the sample 7-base material as an indium

Width of face 50mm, die length 50mm and an indium foil with a thickness of 15 micrometers are made into an anode plate, platinum is used as cathode, and it is concentration as the electrolytic solution. A 0.5 mols [1. ] oxalic acid solution is used, and it is an electrical potential difference. Potentiostatic electrolysis was carried out by 45V, and electrolytic oxidation of the indium foil was carried out. The diameter of the obtained through tube was 50nm.

[0041]

After [ of energization initiation ] several seconds Although 50mA was shown, it was substantially set to 0 after about 60 minutes. The anode plate was pulled up after that and ion exchange water washed. Then, the anode plate front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH

radical was embellished in the inner-wall-of-through-hole side.

[0042]

Creation of the electrolyte membrane made from silicon oxide which obtained the sample 8-base material as silicon

It is width of face on a copper foil electrode. 50mm, die length 50mm, thickness The silicon foil formed by 100 micrometers is made into an anode plate, platinum is used as cathode, and it is concentration abbreviation as the electrolytic solution. 0.3 mols/l. A fluoric acid solution is used and it is an electrical potential difference. Potentiostatic electrolysis was carried out by 40 volts, and electrolytic oxidation of the silicon foil was carried out. The diameter of the obtained through tube was 5nm.

[0043]

Energization initiation aftercurrent value Although 50mA was shown It was substantially set to 0 about 2 hours after., The anode plate was pulled up after that and ion exchange water washed. Then, copper foil was removed, the electrolyte membrane made from silicon oxide was separated, and this electrolyte membrane front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-of-through-hole side.

[0044]

(Example 2)

The fuel cell was constituted using the various electrolyte membranes obtained in the example 1, and the permeability of the existence of generating of a current and the methane by the side of an air pole was measured.

[0045]

Although the mass spectrograph investigated whether methane would be put into a fuel electrode side and methane would penetrate to an air pole side, it is after measurement initiation. Even if about 1 hour passed, detection significant in the engine-performance range of a detector was not completed.

[0046]

However, when carrying out the amperometry, after energization and several seconds, the current was measurable. It is clear that disassembly of methane breaks out and the generated proton is penetrating to the air pole through an electrolyte membrane. Therefore, any electrolyte membrane was found by having high ion selectivity. In addition, the generated current was as follows, respectively.

The bond current was measured for resistance of 1 kilohm outside.

[0047]

Sample 1 0.57mA

Sample 2 0.78mA

Sample 3 0.76mA

Sample 4 0.79mA

Sample 5 0.63mA

Sample 6 0.65mA

Sample 7 0.58mA

Sample 8 0.60mA

(Example 2 of a comparison)

The fuel cell was constituted using Nafion 117, 1135, and 1035, and the permeability of the existence of generating of a current and the methane by the side of an air pole was measured.



[0048]

Methane was put into the fuel electrode side and the mass spectrograph investigated whether methane would penetrate to an air pole side. After measurement initiation About 10 seconds, methane came to be detected and it was detected continuously after that in the elapsed place. Moreover, if water was not used in the case of Nafion, the current did not flow.

[0049]

When it measured by carrying out methane in water at through and a hydrophilic property, the current which had generated the current and was generated was as follows, respectively.

[0050]

Nafion 117 0.5mA

Nafion 1135 0.45mA

Nafion 1035 0.55mA

[0051]

[Effect of the Invention]

As stated above, this invention is the electrolyte membrane for fuel cells which has diameter the through tube of 0.01-150 micrometers prepared by anodizing a metal, and embellished the functional group of proton conductivity in the wall of this through tube. While maintaining proton selectivity highly by carrying out like this, it becomes possible to consider as the electrolyte membrane which thermal resistance is raised, a generation of electrical energy is possible when there are not 100 degrees C or more and \*\*\*\*, and can be used also under the environment of a steam. Moreover, in this invention, by selecting the class and tight ness of a functional group of an electrolyte membrane, coexistence of water stops becoming indispensable and serves as a very realistic fuel cell.

[Brief Description of the Drawings]

[Drawing 1] It is drawing having shown the structure and the principle of operation of a PEFC mold fuel cell.

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## TECHNICAL FIELD

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[Field of the Invention]

It is used inside the fuel cell which is capturing the spotlight especially recently because energy generation effectiveness is high.

[0002]

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## PRIOR ART

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[Description of the Prior Art]

A fuel cell is classified into four kinds according to the class of electrolyte used. It is with a solid acid ghost form fuel cell (SOFC) and a solid-state macromolecule form fuel cell (PEFC) to be classified according to in these four kinds as what is used in a moderate temperature field from a low-temperature field. Moreover, since electrolytic immobilization is easy for these, application to a mobile is also possible, an interest is attracted most and expansion of applicability is considered recently.

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In PEFC, the application as a power source for a small home power source, a portable power source, and mobiles is being developed using the output in low temperature being large, but on

the other hand, development of the ion-selective polyelectrolyte film with unnecessary moisture management with high thermal resistance is called for. Moreover, although the expectation as a power source for pocket devices is growing since the thing of a type which reforms a methanol fuel directly within a cell and obtains hydrogen is easy to miniaturize, the endurance over a methanol is high and development of the polyelectrolyte film with high ion selectivity is called for.

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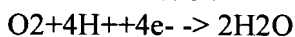
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[0005]

Anode reaction



Cathode reaction



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Although proton selectivity is improved to be sure, since an ingredient is a macromolecule or a macromolecule subject like said Nafion, this proposed electrolyte membrane has the fault of not being made to an elevated temperature 100 degrees C or more. For this reason, it is applicable to the home stationing mold with which the specification of a steam is examined for the effectiveness rise. In addition, service temperature is considered to be 150-250 degrees C in this

case.  
[0009]

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## EFFECT OF THE INVENTION

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### [Effect of the Invention]

As stated above, this invention is the electrolyte membrane for fuel cells which has diameter the through tube of 0.01-150 micrometers prepared by anodizing a metal, and embellished the functional group of proton conductivity in the wall of this through tube. While maintaining proton selectivity highly by carrying out like this, it becomes possible to consider as the electrolyte membrane which thermal resistance is raised, a generation of electrical energy is possible when there are not 100 degrees C or more and \*\*\*\*, and can be used also under the environment of a steam. Moreover, in this invention, by selecting the class and tight ness of a functional group of an electrolyte membrane, coexistence of water stops becoming indispensable and serves as a very realistic fuel cell.

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## TECHNICAL PROBLEM

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### [Problem(s) to be Solved by the Invention]

The place which this invention is made in view of the above-mentioned situation, and is made into the purpose is offer of the electrolyte membrane for fuel cells usable at the temperature of 100 degrees C or more with high and proton selectivity in the electrolyte membrane for fuel cells which uses hydrogen or a methanol as a fuel.

[0010]

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## MEANS

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### [Means for Solving the Problem]

This invention which solves the above-mentioned technical problem has diameter the through tube of 0.01-150 micrometers prepared by anodizing a metal membrane or the silicon film, and is characterized by embellishing the functional group of proton conductivity in the wall of this through tube.

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Moreover, as a functional group of this invention, an OH radical is desirable.

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Moreover, if the electrolyte membrane of this invention is used, since the fuel cell which can be used to an elevated temperature 100 degrees C or more can be created, it becomes usable also as a fixed mold fuel cell in the object for mount, or a home.

[0016]

By this invention, an electrolyte membrane is created by anodic oxidation of a metal membrane or the silicon film because [ of the heat-resistant improvement in the film ]. What can be used as a metal membrane must be what can form a through tube with a diameter of 0.01-150 micrometers by anodic oxidation. It is more desirable than a handling low price, economical efficiency, etc. to use aluminum, titanium, zinc, and the alloy that makes an indium and these a principal component as a metal membrane ingredient. Although a through tube is prepared in such a metal membrane and silicon film according to electrolytic oxidation, the diameter of a through tube is possible by adjusting anodic oxidation conditions, such as an electrical potential difference, an electrode spacing, time amount, and an acid type.

[0017]

In addition, anodic oxidation makes a metal membrane and the silicon film an anode plate, and direct current voltage is impressed in water or the electrolytic solution. At this time, while oxygen usually occurs, according to an electrical potential difference, an acid type, time amount, etc., the through tube of the diameter of a request carries out self-alignment tidily in an anode plate at spacing which is about several 10-100nm.

[0018]

By the way, if the diameter of a through tube is too small, although proton selectivity will improve, passage resistance becomes large, and the function as a cell falls. Moreover, since hydrogen and the methanol used as a raw material will also be passed although passage resistance of a proton decreases if it becomes large on the contrary, a cell property falls. From such a thing, the function as a filter will also be required of an electrolyte membrane. That is, to determine the diameter of a through tube with a raw material is desired. Therefore, although the path near 150nm is sufficient when using a raw material with big molecule size, in the case of a raw material with small molecule size, dozens of nm or less is needed. the need of being referred to as 0.01-1nm when using hydrogen as a raw material -- things are desirable.

[0019]

The functional group of proton conductivity is embellished in an inner-wall-of-through-hole side. As a functional group, it is simple to choose an OH radical, and it is good. Moreover, since spacing of an OH radical is made densely, it can make transfer of a proton good.

[0020]

When a functional group attaches and aluminum is chosen, for example as an electrolyte membrane ingredient as a direction, the front face which includes an inner-wall-of-through-hole side according to electrolytic oxidation is covered with the alumina film. In the case of the alumina film, it is possible to embellish an anion and a cation bordering on the pH= abbreviation 9. Because, pH is charged in  $\text{AlO}_2^-$  in nine or more abbreviation, and an alumina film front face

is charged in aluminum<sup>3+</sup>, when pH is less than abbreviation 9. Therefore, pH is made less than into nine and an OH radical is supplied to an alumina front face.

[0021]

The aluminum film after electrolytic oxidation is first immersed in ion exchange water, into ion exchange water, a nitric acid is added and, specifically, pH is lowered to about four. Then, aqueous ammonia is dropped into ion exchange water, pH is returned to 7, and ion exchange water is exchanged and washed.

[0022]

In addition, when the alumina front face is dry, a good result will be obtained, if the above-mentioned actuation is tried after applying and humidifying steam on this front face.

[0023]

Moreover, if not only an OH radical but a catalyst bed is applied to an inner-wall-of-through-hole side, it is possible it not only does not to let a big molecule pass, but to disassemble a raw material to a proton inside an electrolyte membrane through tube.

[0024]

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## EXAMPLE

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[Example]

Next, this invention is further explained using an example.

(Example 1)

Creation of the electrolyte membrane 1 made from an alumina which obtained the sample 1-base material as aluminum

Aluminium foil with width of face of 50mm, a die length [ of 50mm ], and a thickness of 15 micrometers was made into the anode plate, platinum was used as cathode, using the oxalic acid solution of concentration 0.3 mol/l as the electrolytic solution, potentiostatic electrolysis was carried out on the electrical potential difference of 40 volts, and electrolytic oxidation of the aluminum was carried out.

[0025]

after [ of energization initiation ] several seconds, although the current value became about 1 law by 50mA, it was substantially set to 0mA after about 60 minutes. The anode plate was pulled up and rinsed after that, it exfoliated, the film was dipped in the mixed acid (6wt% sulfuric-acid +1.8wt% hydrochloric acid) about dozens seconds, and it washed in cold water immediately. The diameter of the obtained through tube was about 70nm.

[0026]

Then, the anode plate front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-of-through-hole side.

[0027]

Creation of the electrolyte membrane 2 made from an alumina which obtained the sample 2-base material as aluminum

Aluminium foil with width of face of 50mm, a die length [ of 50mm ], and a thickness of 15 micrometers was made into the anode plate, platinum was used as cathode, using the oxalic acid solution of concentration 0.3 mol/l as the electrolytic solution, potentiostatic electrolysis was carried out on the electrical potential difference of 50 volts, and electrolytic oxidation of the aluminum was carried out.

[0028]

after [ of energization initiation ] several seconds, although the current value became about 1 law by about 60mA, it was substantially set to 0mA after about 60 minutes. The anode plate was pulled up and rinsed after that, it exfoliated, the film was dipped in the mixed acid (6wt% sulfuric-acid +1.8wt% hydrochloric acid) about dozens seconds, and it washed in cold water immediately. The diameter of the obtained through tube was 50nm.

[0029]

Then, the anode plate front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-of-through-hole side.

[0030]

Creation of the electrolyte membrane 3 made from an alumina which obtained the sample 3-base material as aluminum

Aluminium foil with width of face of 50mm, a die length [ of 50mm ], and a thickness of 15 micrometers was made into the anode plate, platinum was used as cathode, using the oxalic acid solution of concentration 0.3 mol/l as the electrolytic solution, potentiostatic electrolysis was carried out on the electrical potential difference of 40 volts, and electrolytic oxidation of the aluminum was carried out.

[0031]

after [ of energization initiation ] several seconds, although the current value became about 1 law by 50mA, it was substantially set to 0mA after about 60 minutes. The anode plate was pulled up and rinsed after that, it exfoliated, the film was dipped in the mixed acid (6wt% sulfuric-acid +1.8wt% hydrochloric acid) about several seconds, and it washed in cold water immediately. The diameter of the obtained through tube was about 1nm.

[0032]

The anode plate was pulled up after that and ion exchange water washed. Then, the anode plate front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-of-through-hole side.

[0033]

Creation of the electrolyte membrane 4 made from an alumina which obtained the sample 4-base material as aluminum

Aluminium foil with width of face of 50mm, a die length [ of 50mm ], and a thickness of 15 micrometers was made into the anode plate, platinum was used as cathode, using an oxalic acid solution with a concentration of 0.3 mols [ /l. ] as the electrolytic solution, potentiostatic electrolysis was carried out by electrical-potential-difference 40V, and electrolytic oxidation of the aluminum was carried out (it is the same as data 1).

[0034]

The film finally obtained was dipped in the mixed acid (6wt% sulfuric-acid +1.8wt% hydrochloric acid) about 1 second, and it washed in cold water immediately. Consequently, when the detailed hole got bored with the last edge of pore and having been measured in TEM, the diameter of the obtained through tube was about 0.5nm.

[0035]

The anode plate was pulled up after that and ion exchange water washed. Then, the anode plate front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-

of-through-hole side.

[0036]

It is creation of the electrolyte membrane made from titanium \*\*\*\* titanium oxide about a sample 5-base material.

Width of face 50mm, die length 50mm and a titanium foil with a thickness of 15 micrometers are made into an anode plate, platinum is used as cathode, and it is concentration as the electrolytic solution. A 0.5 mols [l. ] oxalic acid solution is used, and it is an electrical potential difference. Potentiostatic electrolysis was carried out by 60 volts, and electrolytic oxidation of the titanium foil was carried out. The diameter of the obtained through tube was about 50nm.

[0037]

Several energization initiation second aftercurrent value Although 45mA was shown, it was substantially set to 0 after 65 minutes. The anode plate was pulled up after that and ion exchange water washed. Then, the anode plate front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-of-through-hole side.

[0038]

Creation of the electrolyte membrane made from a zinc oxide which obtained the sample 6-base material as zinc

Width of face 50mm, die length 50mm and a zinc foil with a thickness of 15 micrometers are made into an anode plate, platinum is used as cathode, and it is concentration as the electrolytic solution. A 0.5 mols [l. ] oxalic acid solution is used, and it is an electrical potential difference. By 50 volts, potentiostatic electrolysis was carried out and zinc Tomari electrolytic oxidation was carried out. The diameter of the obtained through tube was about 45nm.

[0039]

Several energization initiation second aftercurrent value Although 50mA was shown, it was substantially set to 0 after 50 minutes. The anode plate was pulled up after that and ion exchange water washed. Then, the anode plate front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-of-through-hole side.

[0040]

Creation of the electrolyte membrane made from indium oxide which obtained the sample 7-base material as an indium

Width of face 50mm, die length 50mm and an indium foil with a thickness of 15 micrometers are made into an anode plate, platinum is used as cathode, and it is concentration as the electrolytic solution. A 0.5 mols [l. ] oxalic acid solution is used, and it is an electrical potential difference. Potentiostatic electrolysis was carried out by 45V, and electrolytic oxidation of the indium foil was carried out. The diameter of the obtained through tube was 50nm.

[0041]

After [ of energization initiation ] several seconds Although 50mA was shown, it was substantially set to 0 after about 60 minutes. The anode plate was pulled up after that and ion exchange water washed. Then, the anode plate front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-of-through-hole side.

[0042]

Creation of the electrolyte membrane made from silicon oxide which obtained the sample 8-base material as silicon

It is width of face on a copper foil electrode. 50mm, die length 50mm, thickness The silicon foil formed by 100 micrometers is made into an anode plate, platinum is used as cathode, and it is concentration abbreviation as the electrolytic solution. 0.3 mols/l. A fluoric acid solution is used and it is an electrical potential difference. Potentiostatic electrolysis was carried out by 40 volts, and electrolytic oxidation of the silicon foil was carried out. The diameter of the obtained through tube was 5nm.

[0043]

Energization initiation after current value Although 50mA was shown It was substantially set to 0 about 2 hours after., The anode plate was pulled up after that and ion exchange water washed. Then, copper foil was removed, the electrolyte membrane made from silicon oxide was separated, and this electrolyte membrane front face was vapor-deposited by Pt to extent which does not bury a through tube. Then, according to the above-mentioned approach, the OH radical was embellished in the inner-wall-of-through-hole side.

[0044]

(Example 2)

The fuel cell was constituted using the various electrolyte membranes obtained in the example 1, and the permeability of the existence of generating of a current and the methane by the side of an air pole was measured.

[0045]

Although the mass spectrograph investigated whether methane would be put into a fuel electrode side and methane would penetrate to an air pole side, it is after measurement initiation. Even if about 1 hour passed, detection significant in the engine-performance range of a detector was not completed.

[0046]

However, when carrying out the amperometry, after energization and several seconds, the current was measurable. It is clear that disassembly of methane breaks out and the generated proton is penetrating to the air pole through an electrolyte membrane. Therefore, any electrolyte membrane was found by having high ion selectivity. In addition, the generated current was as follows, respectively.

The bond current was measured for resistance of 1 kilohm outside.

[0047]

Sample 1 0.57mA

Sample 2 0.78mA

Sample 3 0.76mA

Sample 4 0.79mA

Sample 5 0.63mA

Sample 6 0.65mA

Sample 7 0.58mA

Sample 8 0.60mA

(Example 2 of a comparison)

The fuel cell was constituted using Nafion 117, 1135, and 1035, and the permeability of the existence of generating of a current and the methane by the side of an air pole was measured.

[0048]

Methane was put into the fuel electrode side and the mass spectrograph investigated whether methane would penetrate to an air pole side. After measurement initiation About 10 seconds, methane came to be detected and it was detected continuously after that in the elapsed place.



Moreover, if water was not used in the case of Nafion, the current did not flow.

[0049]

When it measured by carrying out methane in water at through and a hydrophilic property, the current which had generated the current and was generated was as follows, respectively.

[0050]

Nafion 117 0.5mA

Nafion 1135 0.45mA

Nafion 1035 0.55mA

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is drawing having shown the structure and the principle of operation of a PEFC mold fuel cell.

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## CLAIMS

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[Claim(s)]

[Claim 1]

It is an electrolyte membrane for fuel cells about having diameter the through tube of 0.01-150 micrometers prepared by anodizing a metal membrane or the silicon film, and having embellished the functional group of proton conductivity in the wall of this through tube.

[Claim 2]

The electrolyte membrane for fuel cells according to claim 1 whose metal membrane quality of the materials are aluminum, titanium, zinc, and the alloy with which an indium and these are made into a principal component.

[Claim 3]

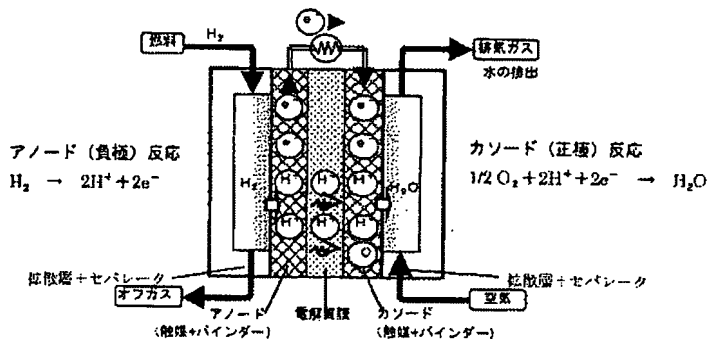
The electrolyte membrane for fuel cells according to claim 1 or 2 whose functional group is an OH radical.

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## DRAWINGS

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[Drawing 1]



[Translation done.]

(19) 日本国特許庁(JP)

(12) 公開特許公報(A)

(11) 特許出願公開番号

特開2004-47206

(P2004-47206A)

(43) 公開日 平成16年2月12日(2004.2.12)

(51) Int.Cl.<sup>7</sup>

H01M 8/02  
C25D 11/00

F I

H01M 8/02 M  
C25D 11/00 304

テーマコード(参考)

5H026

審査請求 未請求 請求項の数 3 O L (全 8 頁)

(21) 出願番号 特願2002-201005 (P2002-201005)  
(22) 出願日 平成14年7月10日(2002.7.10)

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Fターム(参考) 5H026 AA06 AA08 BB10 CX05 EE01  
EE02 HH04

(54) 【発明の名称】 燃料電池用電解質膜

(57) 【要約】

【課題】 水素あるいはメタノールを燃料として用いる燃料電池用電解質膜でプロトン選択性が高く、かつ100℃以上の温度で使用可能な燃料電池用電解質膜の提供である。

【解決手段】 金属膜またはケイ素膜を陽極酸化することにより設けられた直径0.01~150μm貫通孔を有し、該貫通孔の内壁にプロトン伝導性の官能基を修飾したことを特徴とするものである。また、本発明の官能基としてはOH基が好ましい。本発明の金属膜材質として用いるものは陽極酸化により貫通孔を形成しうるものである。より好ましくはアルミニウム、チタン、亜鉛、インジウムやこれらを主成分とする合金である。

## 【特許請求の範囲】

## 【請求項1】

金属膜またはケイ素膜を陽極酸化することにより設けられた直径0.01～150μm貫通孔を有し、該貫通孔の内壁にプロトン伝導性の官能基を修飾したことを燃料電池用電解質膜。

## 【請求項2】

金属膜材質がアルミニウム、チタン、亜鉛、インジウムやこれらを主成分とする合金である請求項1記載の燃料電池用電解質膜。

## 【請求項3】

官能基がOH基である請求項1または2記載の燃料電池用電解質膜。

## 【発明の詳細な説明】

## 【0001】

## 【発明の属する技術分野】

エネルギー発生効率が高いことで最近特に注目を浴びている燃料電池の内部で使用される。

## 【0002】

## 【従来の技術】

燃料電池は使用される電解質の種類により4種類に分類される。この4種類の中で低温領域より中温領域で使用されるものとして分類されるのが固体酸化物形燃料電池(SOFC)と固体高分子形燃料電池(PEFC)とである。また、これらは電解質の固定が容易であることから移動体への適用も可能であり、最近、最も関心を集め、かつ適用範囲の拡大が検討されている。

## 【0003】

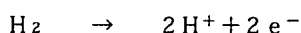
PEFCの場合、低温での出力が大きいことを利用して小型の家庭電源、ポータブル電源、移動体用電源としての用途が開発されつつあるが、その一方で耐熱性が高く水分管理が不要なイオン選択性高分子電解質膜の開発が求められている。また、メタノール燃料を電池内で直接改質し水素を得るタイプのものは小型化が容易であるため、携帯機器用電源としての期待が高まっているが、メタノールに対する耐久性が高く、イオン選択性の高い高分子電解質膜の開発が求められている。

## 【0004】

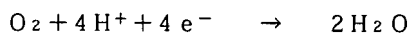
ところで、燃料電池は基本的にはアノード極(燃料極)、カソード極(空気極)、電解質膜から構成されている。図1にPEFCを例に燃料電池の構造と動作原理を特許庁技術調査課による「燃料電池に関する技術動向調査」より引用して示した。アノードは水素から電子を奪いプロトン形成する触媒と燃料である水素のガス拡散層と集電体としてのセパレーターが積層されて構成されている。また、カソードはプロトンと酸素との反応を行わせる触媒と空気の拡散層とセパレーターとが積層されて構成されている。電解質膜は一般にスルホン酸系のプロトン伝導性の高分子電解質膜が用いられている。各電極での反応は以下になる。

## 【0005】

アノード反応



カソード反応



PEFC用の高分子電解質膜として良く知られたものにパーフルオロスルホン酸(商品名:Nafion Dupont社製)などのプロトン伝導性固体高分子膜等がある。こうした膜には、その内壁に遊離のOH<sup>-</sup>基が設けられた直径100nm程度の貫通孔が多数設けられており、このOH<sup>-</sup>基によりプロトンをアノード側よりカソード側に透過させることを特徴としている。しかし、こうした膜はプロトンのみでなく、原料である水素分子やメタノール等をもカソード側に透過させてしまうことが知られている。このようなことが起きると供給された燃料と酸化剤とがカソード側で直接反応してしまっ、エネルギーを電力として出力することができない。したがって、安定した出力を得ることができないという問題が生じる。

## 20 【0006】

こうした問題点を解決するものとして特開2002-110200に開示されたプロトン伝導性膜(電解質膜)がある。このプロトン伝導性膜はプロトン伝導性を維持しつつ、メタノールが該膜を透過するのを抑制することを目的とするものである。

## 【0007】

具体的には、プロトン伝導性ポリマーと特定の重合体との複合体、あるいは、プロトン伝導性ポリマーと特定の重合体とTi、Zr、Al、B、Mo、W、Ru、Ir、GeまたはVの群のいずれかの酸化物との共重合体の複合体であることを特徴とする。

## 【0008】

この提案された電解質膜は、確かにプロトン選択性が改善されているものの、前記ナフィオンと同様に材料が高分子、あるいは高分子主体であることから100℃以上の高温にできないという欠点がある。このため、効率アップのために水蒸気の仕様が検討されている家庭用定置型には適用できなものととなっている。なお、この場合、使用温度は150～250℃と考えられている。

## 40 【0009】

## 【発明が解決しようとする課題】

本発明は上記状況に鑑みてなされたものであり、その目的とするところは、水素あるいはメタノールを燃料として用いる燃料電池用電解質膜でプロトン選択性が高く、かつ100℃以上の温度で使用可能な燃料電池用電解質膜の提供である。

## 【0010】

## 【課題を解決するための手段】

上記課題を解決する本発明は、金属膜またはケイ素膜を陽極酸化することにより設けられた直径0.01～15

0  $\mu$ m貫通孔を有し、該貫通孔の内壁にプロトン伝導性の官能基を修飾したことを特徴とするものである。

【0011】

また、本発明の官能基としてはOH基が好ましい。

【0012】

本発明の金属膜材質として用いるものは陽極酸化により貫通孔を形成しうるものである。より好ましくはアルミニウム、チタン、亜鉛、インジウムやこれらを主成分とする合金である。

【0013】

【発明の実施の形態】

本発明は、金属を陽極酸化することにより設けられた直径0.01~150  $\mu$ m貫通孔を有し、該貫通孔の内壁にプロトン伝導性の官能基を修飾した燃料電池用電解質膜である。こうすることにより、プロトン選択性を高く維持すると共に、耐熱性を向上させ、100℃以上、具体的には水蒸気を使用しうる電解質膜とすることが可能となる。

【0014】

本発明の電解質膜を用いるものは、従来の分類で言うところ、PEFCとSOFCの中間型となる。従来、PEFCでは水分の共存が必須であり、そのため、燃料電池では使用温度に限界があった。しかし、本発明では、電解質膜の官能基の種類と密集度を選定することにより水の共存が必須となくなり、きわめて現実的な燃料電池となる。

【0015】

また、本発明の電解質膜を用いれば、100℃以上の高温まで使用が可能な燃料電池が作成できるため、車載用や家庭での定置型燃料電池としても使用可能となる。

【0016】

本発明で、電解質膜を金属膜やケイ素膜の陽極酸化により作成するのは、膜の耐熱性向上のためである。金属膜として用いるものは陽極酸化により直径0.01~150  $\mu$ mの貫通孔が形成できるものでなければならない。取り扱い安さ、経済性等より、金属膜材料としてはアルミニウム、チタン、亜鉛、インジウムやこれらを主成分とする合金を用いることが好ましい。こうした金属膜やケイ素膜に電解酸化により貫通孔を設けるが、貫通孔の直径は電圧、電極間隔、時間、酸種等の陽極酸化条件を調整することにより可能である。

【0017】

なお、陽極酸化とは金属膜やケイ素膜を陽極として水、あるいは電解液中で直流電圧を印加するものである。このとき、陽極では通常酸素が発生すると共に電圧や酸種、時間等に応じて所望径の貫通孔が数10~100 nm程度の間隔で整然と自己整列する。

【0018】

ところで、貫通孔の直径が小さすぎるとプロトン選択性は向上するものの通過抵抗が大きくなり、電池としての

機能が低下する。また、反対に大きくなるとプロトンの通過抵抗は減少するものの、原料となる水素やメタノールも通過することになるので電池特性は低下する。こうしたことから、電解質膜にはフィルターとしての機能も要求されることになる。即ち、原料により貫通孔の直径を決定することが望まれる。よって、分子サイズの大きな原料を使用する場合は、150 nm付近の径でもよいが、分子サイズの小さな原料の場合は、数十nm以下が必要となってくる。水素を原料として使用する場合は0.01~1 nmとする必要ことが望ましい。

【0019】

貫通孔内壁面にプロトン伝導性の官能基を修飾する。官能基としては、OH基を選択することが簡便でよい。また、OH基の間隔は密にできるので、プロトンの伝達を良好にすることが可能である。

【0020】

官能基のつけ方としては、例えば電解質膜材料としてアルミニウムを選んだ場合、電解酸化により貫通孔内壁面を含む表面はアルミナ膜に覆われる。アルミナ膜の場合、pH=略9を境にしてアニオンやカチオンを修飾することが可能である。というのは、pHが略9以上では、アルミナ膜表面は $AlO_2^-$ に帯電し、pHが略9を下回る場合には $Al^{3+}$ に帯電する。よって、pHを9未満としてアルミナ表面にOH基を供給する。

【0021】

具体的には、まず電解酸化後のアルミニウム膜をイオン交換水に浸漬し、イオン交換水中に硝酸を添加してpHを4程度まで下げる。その後、イオン交換水中にアンモニア水を滴下し、pHを7まで戻し、イオン交換水を取り替え洗浄する。

【0022】

なお、アルミナ表面が乾燥している場合には、該表面にスチームを当て、加湿した上で上記操作を試みると良好な結果が得られる。

【0023】

また、貫通孔内壁面にOH基のみでなく、触媒層を塗布すると、大きな分子を通さないのみならず、電解質膜貫通孔内部で原料をプロトンまで分解することが可能である。

【0024】

【実施例】

次に実施例を用いて本発明をさらに説明する。

(実施例1)

試料1—基材をアルミニウムとして得たアルミナ製電解質膜1の作成  
幅50mm、長さ50mm、厚さ15  $\mu$ mのアルミニウム箔を陽極とし、白金を陰極とし、電解液として濃度0.3mol/lのシュウ酸溶液を用い、電圧40ボルトで定電圧電解してアルミニウムを電解酸化した。

【0025】

通電開始数秒後には、電流値は50mAでほぼ一定となったが、約60分後には実質的に0mAとなった。その後陽極を引き上げ水洗し、膜を剥離して混酸(6wt%硫酸+1.8wt%塩酸)に数十秒ほど浸し即座に水洗いをした。得られた貫通孔の直径は約70nmであった。

#### 【0026】

その後、貫通孔を埋めない程度に、陽極表面をPtで蒸着した。その後、上記の方法に従い貫通孔内壁面にOH基を修飾した。

#### 【0027】

試料2-基材をアルミニウムとして得たアルミナ製電解質膜2の作成

幅50mm、長さ50mm、厚さ15μmのアルミニウム箔を陽極とし、白金を陰極とし、電解液として濃度0.3mol/lのシュウ酸溶液を用い、電圧50ボルトで定電圧電解してアルミニウムを電解酸化した。

#### 【0028】

通電開始数秒後には、電流値は約60mAでほぼ一定となったが、約60分後に実質的に0mAとなった。その後陽極を引き上げ水洗し、膜を剥離して混酸(6wt%硫酸+1.8wt%塩酸)に数十秒ほど浸し即座に水洗いをした。得られた貫通孔の直径は50nmであった。

#### 【0029】

その後、貫通孔を埋めない程度に、陽極表面をPtで蒸着した。その後、上記の方法に従い貫通孔内壁面にOH基を修飾した。

#### 【0030】

試料3-基材をアルミニウムとして得たアルミナ製電解質膜3の作成

幅50mm、長さ50mm、厚さ15μmのアルミニウム箔を陽極とし、白金を陰極とし、電解液として濃度0.3mol/lのシュウ酸溶液を用い、電圧40ボルトで定電圧電解してアルミニウムを電解酸化した。

#### 【0031】

通電開始数秒後には、電流値は50mAでほぼ一定となったが、約60分後には実質的に0mAとなった。その後陽極を引き上げ水洗し、膜を剥離して混酸(6wt%硫酸+1.8wt%塩酸)に数秒ほど浸し即座に水洗いをした。得られた貫通孔の直径は約1nmであった。

#### 【0032】

その後陽極を引き上げイオン交換水で洗浄した。その後、貫通孔を埋めない程度に、陽極表面をPtで蒸着した。その後、上記の方法に従い貫通孔内壁面にOH基を修飾した。

#### 【0033】

試料4-基材をアルミニウムとして得たアルミナ製電解質膜4の作成

幅50mm、長さ50mm、厚さ15μmのアルミニウム箔を陽極とし、白金を陰極とし、電解液として濃度

0.3mol/lのシュウ酸溶液を用い、電圧40Vで定電圧電解してアルミニウムを電解酸化した(資料1と同じ)。

#### 【0034】

最終的に得られた膜を、混酸(6wt%硫酸+1.8wt%塩酸)に1秒ほど浸し即座に水洗いをした。その結果、細孔の最終端に微細な孔があき、TEMにて計測したところ、得られた貫通孔の直径は約0.5nmであった。

#### 10 【0035】

その後陽極を引き上げイオン交換水で洗浄した。その後、貫通孔を埋めない程度に、陽極表面をPtで蒸着した。その後、上記の方法に従い貫通孔内壁面にOH基を修飾した。

#### 【0036】

試料5-基材をチタニウム得た酸化チタン製電解質膜の作成

幅50mm、長さ50mm、厚さ15μmのチタニウム箔を陽極とし、白金を陰極とし、電解液として濃度0.5mol/lのシュウ酸溶液を用い、電圧60ボルトで定電圧電解してチタニウム箔を電解酸化した。得られた貫通孔の直径は約50nmであった。

#### 【0037】

通電開始数秒後電流値は45mAを示したが、65分後に実質的に0となった。その後陽極を引き上げイオン交換水で洗浄した。その後、貫通孔を埋めない程度に、陽極表面をPtで蒸着した。その後、上記の方法に従い貫通孔内壁面にOH基を修飾した。

#### 【0038】

30 試料6-基材を亜鉛として得た酸化亜鉛製電解質膜の作成

幅50mm、長さ50mm、厚さ15μmの亜鉛箔を陽極とし、白金を陰極とし、電解液として濃度0.5mol/lのシュウ酸溶液を用い、電圧50ボルトで定電圧電解して亜鉛箔を電解酸化した。得られた貫通孔の直径は約45nmであった。

#### 【0039】

通電開始数秒後電流値は50mAを示したが、50分後に実質的に0となった。その後陽極を引き上げイオン交換水で洗浄した。その後、貫通孔を埋めない程度に、陽極表面をPtで蒸着した。その後、上記の方法に従い貫通孔内壁面にOH基を修飾した。

#### 【0040】

試料7-基材をインジウムとして得た酸化インジウム製電解質膜の作成

幅50mm、長さ50mm、厚さ15μmのインジウム箔を陽極とし、白金を陰極とし、電解液として濃度0.5mol/lのシュウ酸溶液を用い、電圧45Vで定電圧電解してインジウム箔を電解酸化した。得られた貫通孔の直径は50nmであった。

## 【0041】

通電開始数秒後に 50mAを示したが、約60分後に実質的に0となった。その後陽極を引き上げイオン交換水で洗浄した。その後、貫通孔を埋めない程度に、陽極表面をPtで蒸着した。その後、上記の方法に従い貫通孔内壁面にOH基を修飾した。

## 【0042】

試料8—基材をシリコンとして得た酸化ケイ素製電解質膜の作成

銅箔電極上に幅 50mm、長さ 50mm、厚さ 100 $\mu$ mで設けられたシリコン箔を陽極とし、白金を陰極とし、電解液として濃度約 0.3モル/lのフッ酸溶液を用い、電圧 40ボルトで定電圧電解してシリコン箔を電解酸化した。得られた貫通孔の直径は5nmであった。

## 【0043】

通電開始後電流値は 50mAを示したが、約2時間後に実質的に0となった。その後陽極を引き上げイオン交換水で洗浄した。その後、銅箔を除去し、酸化ケイ素製電解質膜を分離し、貫通孔を埋めない程度に、該電解質膜表面をPtで蒸着した。その後、上記の方法に従い貫通孔内壁面にOH基を修飾した。

## 【0044】

(実施例2)

実施例1において得られた各種電解質膜を用いて燃料電池を構成し、電流の発生の有無と空気極側へのメタンガスの透過性を測定した。

## 【0045】

燃料極側に、メタンガスを入れ、空気極側にメタンガスが透過してくるかどうかを質量分析器により調べたが、測定開始後 約1時間経過しても検知器の性能範囲で、有意な検知はできなかった。

## 【0046】

しかし、電流測定をしたら、通電後、数秒後には、電流が計測できた。メタンガスの分解が起き、発生したプロトンが電解質膜を経て空気極に透過していることは明らかである。よって、いずれの電解質膜も高いイオン選択性を有していることがわかった。なお、発生した電流はそれぞれ以下ようになった。

外部に1キロオームの抵抗をつなぎ電流を測定した。

## 【0047】

試料1 0.57mA

試料2 0.78mA

試料3 0.76mA

試料4 0.79mA

試料5 0.63mA

試料6 0.65mA

試料7 0.58mA

試料8 0.60mA

(比較例2)

ナフィオン117、1135、1035を用いて燃料電池を構成し、電流の発生の有無と空気極側へのメタンガスの透過性を測定した。

## 【0048】

燃料極側に、メタンガスを入れ、空気極側にメタンガスが透過してくるかどうかを質量分析器により調べた。測定開始後 10秒程、経過したところでメタンが検知されるようになり、以後継続的に検知された。また、ナフィオンの場合、水を使用しなければ、電流は流れなかった。

## 【0049】

水にメタンガスを通し、親水性にして計測した場合、電流は発生しており、発生した電流はそれぞれ以下になった。

## 【0050】

ナフィオン117 0.5mA

ナフィオン1135 0.45mA

ナフィオン1035 0.55mA

## 【0051】

【発明の効果】

以上述べたように、本発明は、金属を陽極酸化することにより設けられた直径0.01~150 $\mu$ m貫通孔を有し、該貫通孔の内壁にプロトン伝導性の官能基を修飾した燃料電池用電解質膜である。こうすることにより、プロトン選択性を高く維持すると共に、耐熱性を向上させ、100℃以上、で水が無い場合でも発電ができ、また、水蒸気的环境下でも使用できる電解質膜とすることが可能となる。また、本発明では、電解質膜の官能基の種類と密集度を選定することにより水の共存が必須とならなくなり、きわめて現実的な燃料電池となる。

【図面の簡単な説明】

【図1】PEFC型燃料電池の構造と動作原理を示した図である。

